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USE OF COAL COMBUSTION BY-PRODUCTS FOR SOLIDIFICATION/STABILIZATION OF HAZARDOUS WASTES

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INTRODUCTION

The coal combustion by-product (CCB) industry has been interested in the utilization of CCBs for waste solidification/stabilization for several years. Previous research performed at the Energy & Environmental Research Center (EERC) and cofunded by the U.S. Department of Energy (DOE) and Gas Research Institute (GRI) identified an important stabilization mechanism for elements that exist as oxyanions in aqueous solutions, including arsenic, boron, chromium, molybdenum, selenium, and vanadium. This mechanism is the formation of the mineral ettringite, which has been shown to incorporate oxyanionic species into its structure during the formation process. This mineral was identified in comingled by-products from coal combustion and gasification. Follow-on research at the EERC has focused on ettringite synthesis from laboratory reagents and the determination of potential mechanisms of stabilization through ettringite formation. In numerous unrelated CCB research projects funded by DOE and/or industry, ettringite has been identified as a hydration product in a variety of alkaline CCBs. Reduction in the mobility of several trace elements is commonly noted with the presence of this mineral in hydrated CCBs. The cementitious and pozzolanic properties of coal combustion fly ash that make it useful in concrete also allow it to solidify and chemically immobilize soluble inorganic wastes and organic chemicals. Significant interest exists in using fly ash and clean coal technology by-products for waste stabilization, and several commercial vendors have developed patented processes. Commercial waste stabilization processes typically involve controlled mixing and curing using lime, fly ash, portland cement, and various additives.

The discovery that ettringite formation could be used to remove potentially hazardous oxyanions from solution was made during an EERC research project involving the disposal of coal gasification solid and liquid wastes (1). It was observed that solution concentrations of some potentially toxic trace elements decreased with time during long-term leaching in certain mixtures. At the same time, characterization of solids in the wastes showed the concentration of the mineral ettringite was increasing over time. This observation was a major advancement in waste treatment technology and led to additional research on ettringite. Ettringite is a mineral with the nominal composition $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$. Ettringite is also the family name for a series of related compounds, known as a mineral group or family, which includes the following minerals (1):

Ettringite	$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Charlesite	$\text{Ca}_6(\text{Si},\text{Al})_2(\text{SO}_4)_2(\text{B}[\text{OH}]_4)(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Sturmanite	$\text{Ca}_6\text{Fe}_2(\text{SO}_4)_2(\text{B}[\text{OH}]_4)(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$
Thaumasite	$\text{Ca}_6\text{Si}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$
Jouravskite	$\text{Ca}_6\text{Mn}_2(\text{SO}_4)_2(\text{CO}_3)_2(\text{OH})_{12} \cdot 24\text{H}_2\text{O}$
Bentorite	$\text{Ca}_6(\text{Cr},\text{Al})_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$

There are two technical approaches to the use of ettringite formation for the fixation and removal of trace elements from solution. One approach is the formation of a minimal amount of ettringite in a very large volume of solution to remove trace concentrations of elements such as boron and selenium. An alternate approach using ettringite formation is to solidify the entire mass, thus incorporating the oxyanionic elements of interest into the ettringite structure as a monolith. This approach is more applicable for the treatment of smaller volumes of solutions containing high concentrations of boron and/or selenium, accomplishing two objectives: first, the waste is solidified, and second, the hazardous components of the liquid waste are chemically incorporated into the solid matrix. If the procedure is properly performed, a solid with high compressive strength is produced, incorporating excess alkaline components. This process has the potential to produce a highly stabilized mass for the disposal of high-concentration liquids containing boron, selenium, or any other element capable of substituting into the ettringite structure.

EXPERIMENTAL

Five low-rank coal combustion fly ash samples extensively characterized in previous projects (2) were used as a pool of candidate materials for potential use as waste stabilization agents. Two of these fly ash samples were selected because ettringite formed in the solid in long-term leaching experiments, and an associated reduction in leachate concentration of at least one trace element was noted for each sample. Stabilization experiments were performed using these two samples.

The stabilization experiments were designed to evaluate the removal of relatively high concentrations of boron and selenium from a simulated wastewater. The boron and selenium concentrations were determined from samples of contaminated water from a proprietary source. Sulfate was added as one variable in order to determine if high concentrations of sulfate would impact the ability of the ettringite to include trace elements in its structure. The experiments were carried out in 2-liter containers with a 20-to-1 liquid-to-solid ratio (similar to leaching protocols) and continuous end-over-end agitation over the 60-day duration of the experiment. The stabilization experiments were performed using the following matrix:

TABLE 1

Starting Concentration	Matrix of Experimental Variables	
	Simulated Wastewater A, mg/L	Simulated Wastewater B, mg/L
B	15	15
Se	0.1	0.1
SO ₄ ⁼	0	500

Samples of the liquid phase from each experiment were collected at regular time intervals through the 60 days of the experiment. The rotator was stopped, and after the bulk of the solids had settled, samples were collected using a syringe. The samples were then filtered through a 0.45- μ m filter, acidified with concentrated ultrapure nitric acid to 5%, and stored at 4°C in Teflon bottles until submitted for analysis. The boron concentrations were determined by inductively coupled argon plasma (ICAP) spectrometry, and the selenium concentrations were determined with heated graphite furnace atomic absorption spectrometry (HGA-AAS). A time-concentration comparison was developed as shown in the following section.

RESULTS AND DISCUSSION

All results of the analyses of the liquid samples for the stabilization experiments are presented in Tables 2 and 3. The presence of ettringite in the reacted solids was confirmed by x-ray diffraction.

The two sets of data for each sample indicated similar results for changes in boron and selenium concentrations. Set A for each material used a simulated wastewater with boron and selenium only. Set B for each material used a simulated wastewater with boron, selenium, and sulfate. The starting concentrations of all simulated wastewater components are noted above. The analyses of the liquid samples indicated two different phenomena: 1) an increase in solution concentration of boron and selenium; and 2) solution concentration reduction of boron and selenium approaching 100%.

Results for Ash 2 indicated no reduction in boron or selenium concentrations with time, as was expected. In fact, a slight increase in boron and selenium concentrations over the concentrations in the simulated wastewater was noted. These increases may be a result of additional analyte being leached from the solid sample into the liquid phase, or they may be an artifact of the analytical technique used. Quality control methods included in the analyses indicated that the results are accurate; however, it cannot be confirmed that additional analyte was leached from the solid without additional analysis, which was beyond the scope of this study.

TABLE 2

Analytical Results – Solution Concentrations for Simulated Wastewater Treated with Ash 1

	B, mg/L	% B Reduction	Se, mg/L	% Se Reduction
Solution A				
6 hours	7.87	47.5	0.045	55.0
12 hours	6.01	59.9	0.034	66.0
18 hours	4.54	69.7	0.025	75.0
24 hours (1 day)	3.81	74.6	0.025	75.0
2 days	1.60	89.3	—	—
3 days	0.69	95.4	—	—
4 days	0.44	97.1	—	—
5 days	0.39	94.4	—	—
6 days	0.42	97.2	—	—
7 days (1 week)	0.34	97.7	<0.02	>80
4 weeks	0.30	98.0	0.023	77.0
8 weeks	0.24	98.4	0.021	79.0
Solution B				
18 hours	5.09	66.1	0.025	75.0
7 days (1 week)	0.38	97.5	<0.02	>80.0
4 weeks	0.40	97.3	0.023	77.0
8 weeks	0.20	98.7	0.020	80.0

TABLE 3

Analytical Results – Solution Concentrations for Simulated Wastewater Treated with Ash 2

	B, mg/L	% B Reduction	Se, mg/L	% Se Reduction
Solution A				
18 hours	18.0	-20.0	0.11	-10.0
7 days (1 week)	17.8	-18.6	0.12	-12.0
4 weeks	16.7	-11.3	0.106	-6.0
8 weeks	17.2	-14.7	0.13	-30.0
Solution B				
18 hours	18.3	-22.0	0.13	-30.0
7 days (1 week)	18.6	-24.0	0.12	-12.0
4 weeks	16.9	-12.7	0.105	-5.0
8 weeks	18.4	-22.7	0.13	-30.0

Analytical results of solution concentrations of boron and selenium for Ash 1 indicated a relatively quick and consistent reduction of both elements over time. The concentration reduction for boron was > 95 %, and the concentration reduction for selenium was > 75 %.

The primary question regarding the reported results from the stabilization experiments was why the two samples, both of which were identified as ettringite formers, had different effects on the boron and selenium concentrations in the simulated wastewater. A further review of the available results was performed, leading to the development of several hypotheses to explain the observed phenomena.

The Ash 2 was likely prehydrated before received for analysis, as evidenced by the presence of ettringite in the original sample. Although it appears that additional ettringite was formed over the duration of the stabilization experiments, this proposed prehydration of the material may have resulted in a different ettringite formation mechanism. It is proposed that the fast-forming ettringite was already formed at the beginning of the experiment and the needed elemental components may have been depleted from the solid material. The leachate pH of Ash 2 was only slightly higher than the required 11.5.

In the course of other research performed at the EERC, it was noted that another compound, commonly referred to as monophase ($\text{Ca}_4\text{Al}_2[\text{SO}_4]_x[\text{CO}_3]_{1-x}[\text{OH}]_{12} \cdot 5-8\text{H}_2\text{O}$), appears to be equally important in waste treatment. Monophase is a phase related to ettringite by its common components, Ca, Al, SO_4 , OH, and H_2O , as well as its similar synthesis. It is hypothesized that the formation of monophase and potentially other mechanisms for, or precursors to, ettringite formation may have an impact on the ability of the ettringite formed to sorb other elements such as boron and selenium. The available information is not adequate to evaluate this hypothesis. An analytically intensive laboratory research project could be designed to evaluate ettringite formation mechanisms on the uptake of trace elements and facilitate the development of criteria for identification of CCBs that are the best candidates for use in waste stabilization.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the information obtained in this research:

- CCBs can be useful in the chemical fixation of potentially hazardous trace elements.
- Indication of ettringite formation alone is not adequate for selecting a CCB for waste stabilization applications.
- Moderate sulfate concentrations do not promote or inhibit trace element sorption.
- Ettringite formation mechanisms may impact trace element fixation and need to be elucidated.
- Laboratory demonstration of the CCB with the stabilization process being proposed for demonstration or commercial use is necessary to verify the efficacy of the material and process.
- The final waste form must be evaluated prior to management according to the required regulatory procedures.

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